THE EISENHOWER LIBRARY
3 1151 02695 7385

174, 294.

Library

of the

Johns Hopkins University

A Study of the Reactions of Normal Butyl Mercaptan and Some of its Derivatives

A DISSERTATION

Submitted to the Board of University Studies of the Johns Hopkins University in conformity with the requirements for the Degree of Doctor of Philosophy

BY

Thos. C. Whitmer, Jr.

June, 1920.

174.294.

Contents

Abstract 3
Introduction 4
Experimental
Reaction with HCl and NaOH 9
Reaction with Alkaline and Tetrone 11
Reaction of Acyl Chloride 12
Discussion 17
Bibliography 20

The last class of compounds studied was the alcohol formed by the action of ketyl magnesium with chloroacetic.

$$R_1R_2R'_2C(OH)CH_2CH_2OH + MgCl$$

All of the compounds obtained were liquids, some of them having very high boiling points. They decomposed slightly under reduced pressure. In order to identify these products other than by their boiling points, density, and index of refraction it was very desirable to obtain in some manner crystalline derivatives. The class of compounds of this sort which are usually thought of in connection with the sulphides are the sulphones, which are formed by the oxidation of the sulphide. These compounds are crystalline and can be obtained in a very pure condition by recrystallization, usually from water.

The straight chain sulphides, such as $C_6H_5SCH_2CH_2SC_6H_5$, the corresponding sulphone can be obtained very easily and in good yields by the oxidation of the sulphide with either fuming nitric acid or a permanganate mixture. In the first method the sulphide is dissolved slowly into the acid and the mixture is kept cold with water; while in the second method a water solution of the oxidizing mixture and the sulphide are boiled.

For the hexagonal and monoglycol sulfur oxidizing methods must be employed. Therefore the molecule is completely oxidized by nitric or permanganate acid. Several methods were tried for the oxidation of these compounds. The sulphide was mixed with a 5% solution of permanganate and a 5% solution of sulphuric acid slowly dropped into the mixture; the mixture boiled but not well stirred. The results of this process was also tried. Another method for the oxidation of these compounds was to dissolve the sulphide in cold glacial acetic acid and add to the mixture, keeping it well stirred.

---

1. Norman, Ber. 73, 1511, (1940).

finely ground ammonium chloride in small portions. This test method was reliable to test with distilled of the type [illegible]; but on those who are much easier accompanied by solutions than either the acetylene or acetylene [illegible] may not possess any it should not be just as applicable. Those metals related molybdenum with the sulphides obtained by the action of hydrogen sulphide on the corresponding sulphides formed from balance and acetylene in all cases the solvents appeared to have been retained by the sulphonic acid, as no sulphones could be obtained.

As crystalline derivatives of these compounds could not be obtained from oil, it was thought that will would yield metallic derivatives. For this purpose it was attempted to combine all of the sulphides with corrosive sublimate. Mercury was chosen simply because, with the soluble exceptions of gold and platinum, these derivatives are the most stable. The sulphide was used instead of the chloride for the reason that the latter compound and the derivatives are more soluble in pyridine and we [illegible] and acetone.

It was thought that the corrosive sublimate would combine with these sulphides in the ratio of one to one, as for example $Ta^{2}S_{5}.HgCl_{2}$ and $Ta_{2}S_{5}.2HgCl_{2}$. Except for the two sulphides, $Ta_{2}S_{5}$ and $Ta_{2}S_{5}$, this did not hold given. In all cases the mercuric [illegible] lost one atom of [illegible], and two of the [illegible] were present in the resulting compound for each sulphide atom present. Also if the sulphide treatment a replaceable hydrogen atom is all cases

---

1. Pelletier. Ann. [illegible], 1834, [illegible].

[illegible]

Reactions with Allyl Halides

Benzyl ethyl sulphide $C_6H_5CH_2SC_2H_5$

To a solution of 11 grams of caustic potash and 19 grams of benzyl mercaptan in 50cc of alcohol is added slowly 22 grams of ethyl iodide, and the mixture is allowed to stand for several hours; it is then heated for an hour on a boiling water bath under reflux. The mixture is then diluted with a large volume of water, the oily layer separated, [illegible] dilute caustic potash solution, and finally water; it is dried over solium chloride and distilled. The sulphide is a colourless liquid distilling at 240-241° at atmospheric pressure. Yield 18 grams.

Index of refraction at 20° 1.5527

Density [illegible] and [illegible]

Benzyl allyl derivative $C_6H_5CH_2SC_3H_5$

To 4 grams of [illegible] mercaptan in 50cc of alcohol was added a gram of the solution and the mixture well shaken. In a few minutes all of the mercaptan [illegible] and the solution allowed to stand for a short time. It [illegible] and with stirring, nitrogen. The crystals separating are filtered, washed with alcohol and dried. There are small white plates melting at 111.

Analysis

No. of sample, [illegible] gm.; wt. of CO_2, [illegible] gm.; CO_2 found [illegible] CO_2 calculated 83.5%.

No. of sample, [illegible] gm.; wt. of $BaSO_4$, [illegible] gm.; S found [illegible] S calculated [illegible].

a 10% yield was obtained.